

Monosize Polystyrene Microbeads by Dispersion Polymerization

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SYNOPSIS

Monosize polystyrene microbeads were prepared by dispersion polymerization in different alcohol/water media. Azobisisobutyronitrile and polyacrylic acid were utilized as initiator and steric stabilizer, respectively. The polymerizations were performed in three kinds of dispersion media having different polarities: isopropanol/water, 1-butanol/water, and 2-butanol/water. The effects of initiator and stabilizer concentrations, alcohol/water ratio, and monomer/dispersion medium ratio on the size and monodispersity of the polymeric microbeads were investigated. By dispersion polymerization, polystyrene (PS) microbeads were obtained in the size range of 1.0–4.0 μm with narrow size distribution or in the monosize form. The average size and size distribution of microbeads decreased with increasing polarity of the dispersion medium. The average size and size distribution increased with increasing initiator concentration in all dispersion media. The increase in the stabilizer concentration in homogeneous dispersion media resulted in a decrease in average size and size distribution of the microbeads. A clear increase was observed in the average size with increasing monomer/dispersion medium ratio. Isopropanol/water dispersion medium provided monosize microbeads with higher values of monomer/dispersion medium ratio. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Many applications in the biomedical field, information industry, and microelectronics require the use of polymeric particles of controlled size and surface properties. Traditionally, micron-size particles have been prepared by suspension polymerization, where monomer droplets are broken into the micron-size range within a dispersion medium by homogenization in the presence of a stabilizer, and subsequently are polymerized by using a monomer phase soluble initiator. This technique is usually used for the production of spherical polymeric particles between about 50–1000 μm . A wide particle size distribution is usually observed because of inherent size distribution in the mechanical homogenization step and because of the coalescence problem faced in this type of polymerization.

Typically, polymer latices containing uniform polymeric particles in the submicron-size range are produced by emulsion polymerization. In this process the monomer is present in the form of large droplets suspended in a dispersion medium that contains both an initiator and an emulsifier. Here, the emulsifier molecules are dissolved in the medium (i.e., usually water) in concentrations above a critical level, and they associate with one another to form so-called "micelles." The product of this process is monosize polymer particles in the submicron-size range. The classical emulsion polymerization process is convenient for producing spherical polymeric particles of submicron size with extreme uniformity in size up to about 0.1 μm .

The "swollen emulsion polymerization" developed by Ugelstad and his coworkers was the first successful technique for producing monosize polymeric particles of micron size usually in the range of 0.2–1.5 μm .^{1–4} Micron-size particles as large as 50 μm may be obtained by a multistage process; however, this procedure is very tedious and difficult to carry out.^{3–6} By following a similar technique, Love-

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lace et al. were also able to grow polymeric particles in the micron-size range aboard the space shuttle in microgravity.⁷ If polymerization is initiated in the monomer phase, the resultant average size of the polymer particles can be increased significantly.^{1,2,8,9}

Micron-size monosize polymeric microbeads have also been prepared by dispersion polymerization technique.¹⁰⁻²¹ This process involves the polymerization of a monomer dissolved in a solvent or solvent mixture in the presence of a steric stabilizer. There is initially only one phase where the monomer and the stabilizer molecules are dissolved. Homogeneous nucleation of particles from the medium in a manner similar to the particle formation process in emulsion polymerization takes place. Therefore the growing particles are separated from the medium when the polymerization progresses. A two phase system is obtained at the end of the polymerization. The amount of monomer and the nature of the stabilizer in maintaining the colloidal stability of growing particles strongly affects the final size and size distribution of the particles. Barrett has prepared polymethyl methacrylate monosize microbeads in hydrocarbon media.^{11,12} Almog et al. have reported the preparation of monosize polystyrene and polymethyl methacrylate microbeads up to 5 μm by dispersion polymerization.^{13,14} Corner has described polystyrene microbeads produced in aqueous ethanol media using polyacrylic acid as the steric stabilizer.¹⁵ Ober and his coworkers have produced monosize polystyrene microbeads up to 9 μm by polymerization of styrene in a variety of solvent systems (e.g., 2-methoxyethanol/ethanol) by using different non-ionic cellulosic polymers as steric stabilizers (e.g., hydroxypropylcellulose) with no charged cosurfactants.²²⁻²⁵ They were also successful in forming large monosize copolymer microbeads by dispersion polymerization in the presence of polyacrylic acid as a steric stabilizer.²⁴ Paine et al. studied dispersion polymerization of styrene in alcoholic media in the presence of poly(*N*-vinyl pyrrolidone) as a steric stabilizer.²⁶ They have reported the production of monosize polymer microbeads up to 18 μm in size. Paine has also proposed a simple mathematical model to predict the particle size in dispersion polymerization of styrene in polar solvents.²⁷ Okubo et al. have reported preparation of monosize polymer microbeads having chloromethyl groups by following two-step polymerization in a dispersion medium consisting of water/ethanol mixtures.²⁸

In our recent related studies, we followed a similar technique in order to obtain monosize polystyrene microbeads with different surface groups for diverse biomedical applications.²⁹ In this study, styrene was

polymerized in a medium consist of isopropanol/water, 1-butanol/water, or 2-butanol/water. Polyacrylic acid was used as a steric stabilizer with a disperse phase soluble initiator (i.e., AIBN). This paper gives the detailed procedure, and presents the effects of several parameters on final size and monodispersity of the polystyrene microbeads.

EXPERIMENTAL

Materials

Styrene (S) (Yarpet A. S., Turkey) was treated with aqueous NaOH to remove the inhibitor, and stored

Table I Polymerization Conditions

Initiator Concentration (mol %)	Stabilizer Concentration (g/dL)	Alcohol/Water Ratio (mL/mL)	Monomer/Dispersion Medium Ratio (mL/mL)
0.5	1.0	70/30	1.0/10.0
1.0	1.0	70/30	1.0/10.0
2.0	1.0	70/30	1.0/10.0
0.5	1.0	90/10	1.0/10.0
1.0	1.0	90/10	1.0/10.0
2.0	1.0	90/10	1.0/10.0
1.0	0.5	70/30	1.0/10.0
1.0	1.0	70/30	1.0/10.0
1.0	2.0	70/30	1.0/10.0
1.0	0.5	90/10	1.0/10.0
1.0	1.0	90/10	1.0/10.0
1.0	2.0	90/10	1.0/10.0
1.0	1.0	100/0	1.0/10.0
1.0	1.0	90/10	1.0/10.0
1.0	1.0	80/20	1.0/10.0
1.0	1.0	70/30	1.0/10.0
1.0	1.0	60/40	1.0/10.0
1.0 ^a	1.0	70/30	1.0/10.0
1.0 ^a	1.0	70/30	1.5/10.0
1.0 ^a	1.0	70/30	2.0/10.0
1.0 ^a	1.0	70/30	2.5/10.0
1.0 ^b	1.0	90/10	1.0/10.0
1.0 ^b	1.0	90/10	1.5/10.0
1.0 ^b	1.0	90/10	2.0/10.0
1.0 ^b	1.0	90/10	2.5/10.0

Temperature: 70°C; shaking rate: 100 cpm; total reaction volume: 55 mL. Dispersion medium: alcohol + water; alcohols: isopropanol, 1-butanol, 2-butanol.

^a These experiments were carried out with only isopropanol.

^b These experiments were carried out with isopropanol, 1-butanol, and 2-butanol. The amount of initiator was kept constant at 0.07 g in the experiments carried out with 2-butanol.

Table II Some Physical Properties of Constituents Used in Polymerizations

	Solubility of Water in Alcohol (wt %, 20°C)	Solubility Parameter (cal/cm ³) ^{1/2}	Dielectric Constant	Polarizability	Dipole Moment (Debye)
Water	—	23.4	78.5	1.45	1.84
Iso-PrOH	Infinite	11.5	18.3	6.97	1.66
1-BuOH	20.1	11.4	17.1	8.88	1.66
2-BuOH	35.7	10.8	15.8	—	—
Styrene	—	9.30	—	15.0	—

in a refrigerator until used. The initiator was 2,2'-azobisisobutyronitrile (AIBN, BDH Chemicals Ltd., UK). Isopropanol, 1-butanol, and 2-butanol were obtained from Merck A. G. (Germany) and were used in the dispersion media without further purification.

Polyacrylic acid (PAA) was used as the steric stabilizer. PAA was prepared by solution polymerization of acrylic acid (AA, BDH Chemical Ltd., 60 mL) in 1,4-dioxane (BDH Chemical Ltd., 140 mL) by using AIBN (0.06 g) as an initiator at 80°C for 8 h under nitrogen atmosphere in a magnetically stirred, sealed cylindrical polymerization reactor. PAA was precipitated by pouring the final solution into an excess of petroleum ether. The polymer was dried at room temperature for 24 h. The viscosity-average molecular weight measured in 1,4-dioxane at 25°C was 1.5×10^4 .

Preparation of PS Microbeads

Glass, sealed cylindrical vessels (100 mL) were used for polymerizations. The vessels containing the polymerization media (55 mL) were placed in a temperature controlled water bath at 70°C, and shaken horizontally at 100 cycles/min for 24 h. Reactions were conducted in three different dispersion media: isopropanol/water, 1-butanol/water, and 2-butanol/water. The initiator and stabilizer concentrations, the alcohol/water ratio, and the monomer/dispersion medium volumetric ratio were changed to obtain the effects of these parameters on the size and size distribution of the PS microbeads. The experimental conditions are given in Table I.

Particle Size Analysis

The average size and size distributions of the PS microbeads were evaluated using a scanning electron

Table III Solubility Data of Dispersion and Polymerization Media

Medium	Alcohol/ Water Ratio (mL/mL)	Dispersion Medium			Polymerization Medium ^a		
		Solubility Parameter (cal/cm ³) ^{1/2}	20°C	70°C	Solubility Parameter (cal/cm ³) ^{1/2}	20°C	70°C
Iso-PrOH/ water	70/30	16.03	H	H	15.55	H	H
1-BuOH/ water	70/30	—	HT (86.0/14.0)	HT (87.0/13.0)	—	HT (80.0/20.0)	HT (83.5/16.5)
2-BuOH/ water	70/30	15.68	H	HT (97.5/2.5)	—	HT (82.0/18.0)	HT (84.0/16.0)
Iso-PrOH/ water	90/10	13.18	H	H	12.85	H	H
1-BuOH/ water	90/10	13.10	H	H	12.81	H	H
2-BuOH/ water	90/10	12.64	H	H	12.55	H	H

H: homogeneous medium; HT: heterogeneous medium. The numbers in parentheses show the volumetric ratio of upper (light, apolar) phase to lower (heavy, polar) phase.—Solubility parameter is not calculated for the heterogeneous medium.

^a Monomer concentration was fixed to 10% (v/v) as in the polymerization experiments.

microscope (SEM, Model Leitz-AMR 1000 Raster Electronen Microscope, Frankfurt, Germany). The latex solution containing the microbeads was spread onto a metal disk and the solvent (i.e., water and alcohol) was evaporated at room temperature. The dried microbeads were coated with a thin layer (about 100 Å) of gold in vacuum. Three separate photographs (each containing 50–300 beads) were taken for each latex sample with 2500–2800 magnification. The size of the microbeads was measured on the photographs.

SOLUBILITY EXPERIMENTS

The dispersion media used in this study were prepared by mixing three different alcohols (i.e., isopropanol, 1-butanol, and 2-butanol) with water. In the case of lower water contents, either “the dis-

persion medium” (the medium containing only alcohol and water) or “the polymerization medium” (obtained by addition of monomer to the dispersion medium) were completely miscible and showed homogeneous character. However, two phase formation was observed in some of the dispersion or reaction media prepared by mixing 1-butanol and 2-butanol with a large amount of water. To obtain the relative volumes of the phases in two phase systems, the solubility experiments were carried out. The sealed, cylindrical measuring tubes (100 mL), were placed in a temperature controlled water bath. The alcohol/water or alcohol/water and monomer were mixed at the desired ratio and shaken well. The tubes were kept in the water bath for 24 h at constant temperature. Then the volumes of the upper (light) and the lower (heavy) phases were measured. The solubility experiments were conducted at two different temperatures, 20 and 70°C.

Table IV Effects of Initiator Concentration on Average Size and Size Distribution

Dispersion Medium: Isopropanol/Water							
Alcohol/Water Ratio (mL/mL)	Initiator Conc. (mol %)	D (µm)	Dv (µm)	SD (µm)	CV (%)	Size Range (µm)	SSA (m ² /g)
70/30	0.50	1.37	1.37	—	—	MS	4.38
	1.00	1.46	1.46	—	—	MS	4.11
	2.00	1.46	1.46	—	—	MS	4.11
90/10	0.50	1.62	1.62	—	—	MS	3.70
	1.00	1.89	1.89	—	—	MS	3.17
	2.00	1.89	1.89	—	—	MS	3.17
Dispersion Medium: 1-Butanol/Water							
70/30	0.50	1.87	1.88	0.183	9.810	1.33–2.00	3.16
	1.00	2.40	2.43	0.297	12.39	1.75–2.75	2.43
	2.00	2.80	2.89	0.541	19.33	2.19–4.11	1.99
90/10	0.50	1.82	1.82	—	—	MS	3.30
	1.00	2.17	2.26	0.477	21.99	1.03–2.56	2.57
	2.00	2.60	2.92	0.718	27.60	1.03–3.56	1.94
Dispersion Medium: 2-Butanol/Water							
70/30	0.50	1.54	1.54	—	—	MS	3.90
	1.00	1.86	1.86	0.075	4.00	1.84–2.11	3.21
	2.00	1.95	1.95	0.104	5.31	1.79–2.05	3.06
90/10	0.50	1.62	1.61	—	—	MS	3.70
	1.00	2.34	2.41	0.429	18.32	1.35–2.70	2.43
	2.00	2.86	3.07	0.672	23.49	1.35–4.32	1.87

D: average diameter; Dv: volume average diameter; SD: standard deviation; CV: coefficient of variation; SSA: specific surface area; MS: monosize microbeads (CV < 1.0%).

RESULTS AND DISCUSSION

Monosize microbeads have been prepared in a wide variety of solvent combinations by dispersion polymerization.¹⁰⁻²⁸ The polarity of the dispersion medium is one of the most important parameters that controls the average size and the monodispersity of the polymeric microbeads.^{22,23,26-28} Note that in the dispersion polymerization, monomer, initiator, and stabilizer are all soluble in the dispersion medium, and solubilities are directly related to polarity of the dispersion medium.

As we have observed in our preliminary studies, solubility of styrene in the dispersion media consisting of alcohol/water mixtures strongly depend on the alcohol type, water content of the dispersion medium, and solubility of water in alcohol. Therefore, we have prepared different dispersion media having different polarities by changing the alcohol type and water content. Three different alcohols,

namely, isopropanol (Iso-PrOH), 1-butanol (1-BuOH), and 2-butanol (2-BuOH) were used. It should be pointed out that the linear alcohols containing more than four carbon atoms are not proper to prepare monosize polystyrene microbeads. The average size of the microbeads decreases with increasing hydrocarbon chains in the presence of pure, linear alcohols containing more than four carbon atoms.²⁶ In addition, it is very difficult to adjust the polarity of the dispersion medium by changing the amount of water with these higher alcohols, because of the very low solubility of water, which is an important component of the dispersion medium in achieving microbead formation and monodispersity.

In this study, the solubility parameter was considered as a measure of polarity of the dispersion medium. Some physical properties of the main constituents used in the polymerizations are given in Table II.³⁰⁻³² The solubility properties of the dispersion and polymerization media prepared by using

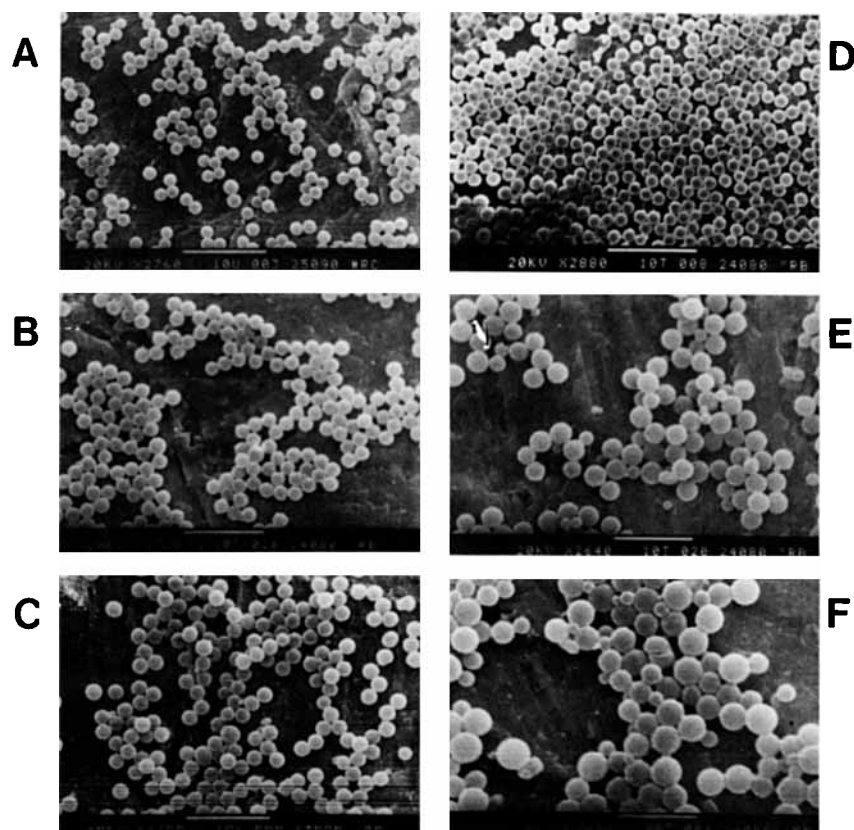


Figure 1 SEM photographs of microbeads with different initiator concentrations (in 2-BuOH/water dispersion medium): (A) 0.5% AIBN, 70/30 2-BuOH/water; (B) 1.0% AIBN, 70/30 2-BuOH/water; (C) 2.0% AIBN, 70/30 2-BuOH/water; (D) 0.5% AIBN, 90/10 2-BuOH/water; (E) 1.0% AIBN, 90/10 2-BuOH/water; (F) 2.0% AIBN, 90/10 2-BuOH/water.

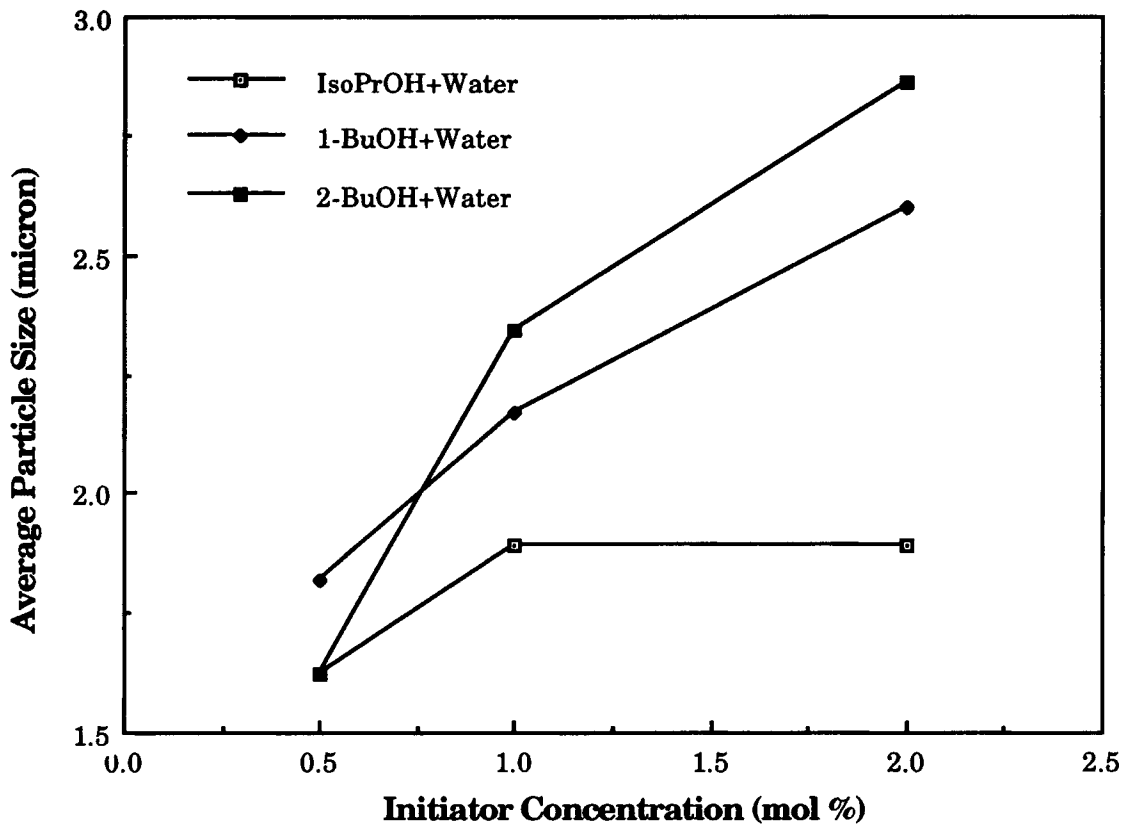


Figure 2 Effect of initiator concentration on average particle size (alcohol/water ratio: 90/10).

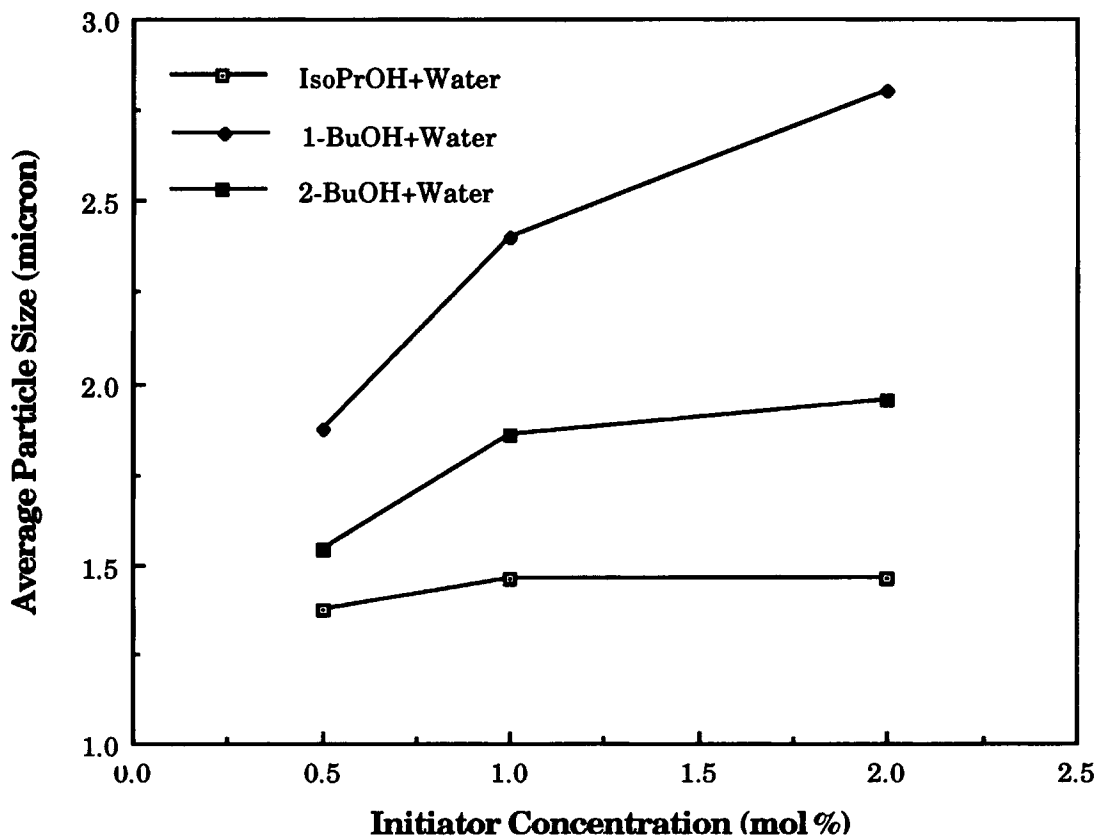


Figure 3 Effect of initiator concentration on average particle size (alcohol/water ratio: 70/30).

different amounts of alcohols, water, and monomer were evaluated by using the data obtained in the solubility experiments and the literature data, and are presented in Table III.

The effects of initiator and stabilizer concentrations, alcohol/water ratio, and monomer/dispersion medium ratio on the final size and monodispersity of the PS microbeads prepared in this study are presented below in four different sections.

Effect of Initiator

In this group of experiments, the effect of initiator (i.e., AIBN) concentration on dispersion polymerization of styrene was investigated. Polymerizations were performed; with three different AIBN concentrations (i.e., 0.5, 1.0, and 2.0 mol %); within three dispersion media (i.e., Iso-PrOH/water, 1-BuOH/water, and 2-BuOH/water); with two different al-

cohol/water ratios (i.e., 70/30 and 90/10); at a constant stabilizer (i.e., PAA) concentration of 1.0 g/dL; and at a constant monomer/dispersion medium ratio of 1.0/10.0. Table IV gives the data obtained in this group of experiments. The SEM photographs of microbeads with different initiator concentrations, in 2-butanol/water dispersion medium are given as an example in Figure 1. The variations of average particle diameter with initiator concentration for apolar (i.e., 90/10 alcohol/water ratio) and polar (i.e., 70/30 alcohol/water ratio) dispersion media are given in Figures 2 and 3, respectively.

As seen here, the average particle size increases with increasing initiator concentration for all dispersion media. This is an expected behavior as also discussed in the literature.²⁵ The increase in the initiator concentration causes an increase in the number of free radicals for polymerization. In other words, polymerization starts with more radicals per

Table V Effects of Stabilizer Concentration on Average Size and Size Distribution

Dispersion Medium: Isopropanol/Water							
Alcohol/Water Ratio (mL/mL)	Stabilizer Conc. (mol %)	D (μm)	Dv (μm)	SD (μm)	CV (%)	Size Range (μm)	SSA (m^2/g)
70/30	0.50	1.47	1.47	—	—	MS	4.08
	1.00	1.46	1.46	—	—	MS	4.11
	2.00	1.08	1.08	—	—	MS	5.56
90/10	0.50	2.50	2.50	—	—	MS	2.40
	1.00	1.89	1.89	—	—	MS	3.17
	2.00	1.36	1.36	—	—	MS	4.41
Dispersion Medium: 1-Butanol/Water							
70/30	0.50	3.04	3.05	0.215	7.06	2.66–3.46	1.96
	1.00	2.40	2.43	0.297	12.39	1.75–2.75	2.43
	2.00	2.12	2.24	0.496	23.40	1.56–3.11	2.55
90/10	0.50	2.26	2.33	0.452	20.01	1.25–2.75	2.49
	1.00	2.17	2.26	0.477	21.99	1.03–2.56	2.57
	2.00	2.16	2.17	0.143	6.61	1.82–2.33	2.75
Dispersion Medium: 2-Butanol/Water							
70/30	0.50	2.05	2.05	0.098	4.78	1.82–2.07	2.92
	1.00	1.86	1.86	0.075	4.00	1.84–2.11	3.21
	2.00	1.32	1.32	—	—	MS	4.55
90/10	0.50	2.42	2.48	0.409	16.92	1.35–2.70	2.37
	1.00	2.34	2.41	0.429	18.32	1.35–2.70	2.43
	2.00	2.23	2.29	0.411	18.43	1.35–2.70	2.55

D: average diameter; Dv: volume average diameter; SD: standard deviation; CV: coefficient of variation; SSA: specific surface area; MS: monosize microbeads (CV < 1.0%).

unit volume in the case of high initiator concentration. This leads to lower molecular weight polymeric chains, which are more soluble in the medium. Note that in dispersion polymerization, nucleation occurs when the polymer chains reach a certain molecular weight at which they become insoluble in the dispersion medium. At high initiator concentration, due to low concentration of high molecular weight chains in the medium, fewer polymerization nuclei are produced, which leads to a lower number of microbeads but with larger size.

Two different dispersion media were utilized to examine the effect of initiator with each alcohol/water system. The dispersion medium containing 70% alcohol and 30% water may be considered a more polar medium compared to that containing 90% alcohol and 10% water (see Table III). As seen in Figure 2 the average particle size generally obeyed

the following order according to the type of dispersion medium with 90/10 alcohol/water ratio.

2-BuOH/water > 1-BuOH/water

> Iso-PrOH/water.

As seen in Table III, both the dispersion and polymerization media are homogeneous for all alcohol types with 90/10 alcohol/water ratio. Therefore, it was possible to estimate the solubility parameters of both the dispersion and polymerization media. The results obtained at constant AIBN concentration for 90/10 alcohol/water ratio indicated that the average particle size increased with decreasing polarity (or decreasing the initial solubility parameter of the dispersion or polymerization medium). The largest microbeads were obtained in 2-BuOH/

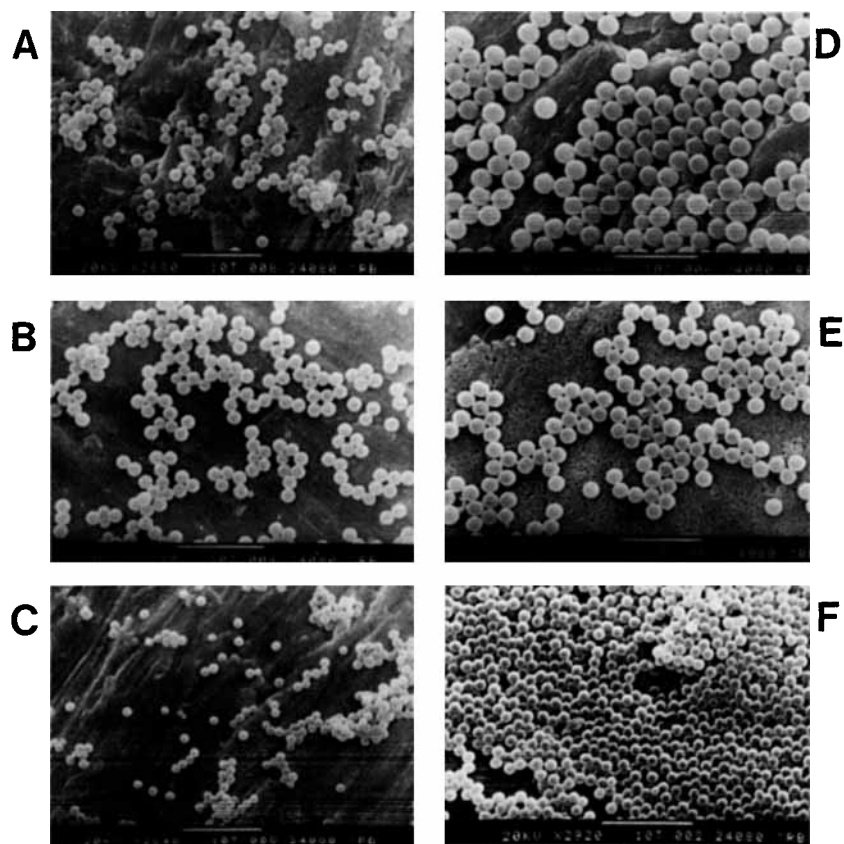


Figure 4 SEM photographs of microbeads with different stabilizer concentrations (in Iso-PrOH/water dispersion medium): (A) 0.5 g PAA/dL, 70/30 Iso-PrOH/water; (B) 1.0 g PAA/dL, 70/30 Iso-PrOH/water; (C) 2.0 g PAA/dL, 70/30 Iso-PrOH/water; (D) 0.5 g PAA/dL, 90/10 Iso-PrOH/water; (E) 1.0 g PAA/dL, 90/10 Iso-PrOH/water; (F) 2.0 g PAA/dL, 90/10 Iso-PrOH/water.

water medium, which has the lowest solubility parameter (the lowest polarity).

As seen in Figure 3 the results obtained in the media with 70/30 alcohol/water ratio were different. The largest microbeads were obtained in the 1-BuOH/water medium, not in the 2-BuOH/water medium. It can be explained by the heterogeneous character (two phase formation) of the polymerization medium for these two alcohols (1-BuOH and 2-BuOH). Note that Iso-PrOH/water medium was homogeneous with 70/30 alcohol/water ratio. The volumetric ratio values of apolar phase to polar phase were very close in 1-BuOH/water and 2-BuOH/water systems in the existence of styrene monomer (Table III). The alcohol content was higher in the upper phase relative to that of the heavy one. On the other hand, the solubility of water in 1-BuOH was less than that in 2-BuOH (Table II). Then, it was expected that the light phase in the 1-BuOH/water dispersion medium contained a lesser amount of water compared to the water content of the light phase in the 2-BuOH/water system. It was expected that most of the hydrophobic styrene

monomer was preferentially collected in the light phase (i.e., larger volume fraction and more apolar), in 1-BuOH/water and 2-BuOH/water dispersion media. Some of the stabilizer also passed to the heavy phase (i.e., mostly water and more polar). The polymerization occurred in the light phase having more apolar character relative to the heavy one, with higher monomer/dispersion medium ratio and lower stabilizer concentration. Therefore, larger microbeads were obtained in the relatively apolar light phase. The light phase in the 1-BuOH/water system having more apolar character provided larger beads relative to the light phase in the 2-BuOH/water system. Both the dispersion and polymerization media were homogeneous in the Iso-PrOH/water system with 70/30 alcohol/water ratio and the smallest beads were obtained in this most polar medium at constant AIBN concentration.

Effect of Stabilizer

In this group of experiments, the effect of stabilizer (i.e., PAA) on dispersion polymerization of styrene

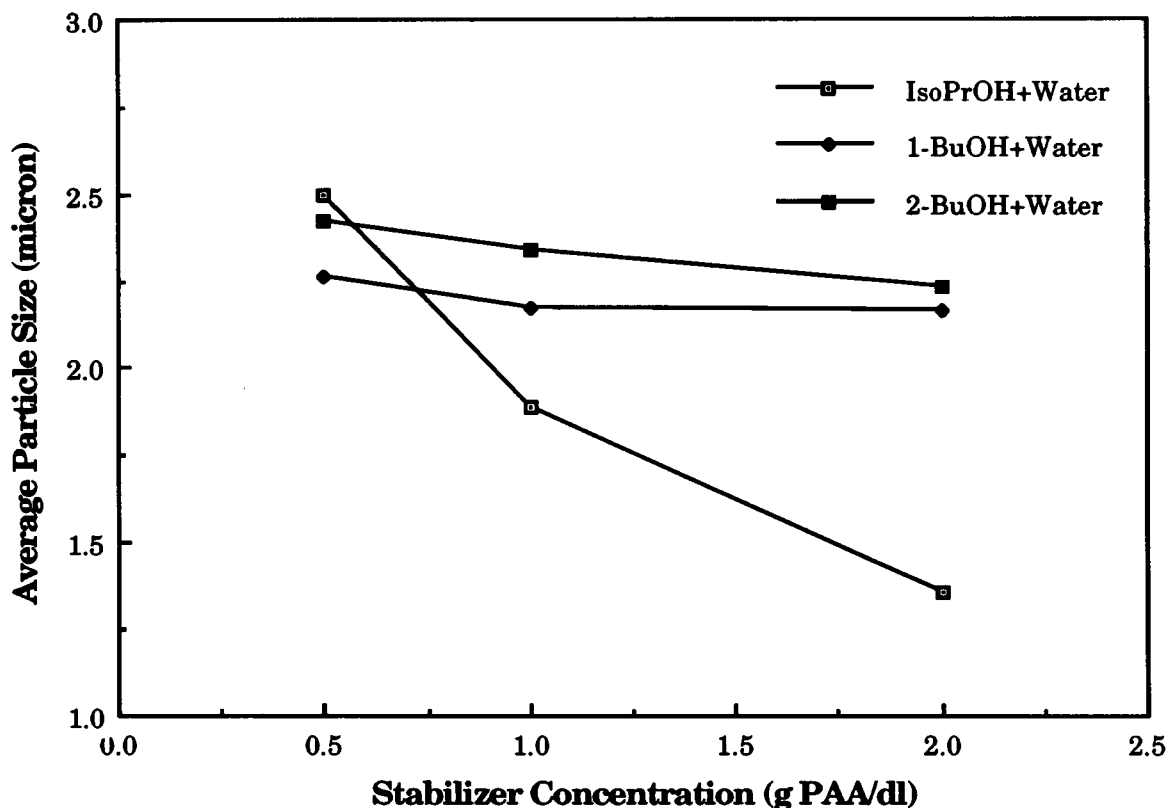


Figure 5 Effect of stabilizer concentration on average particle size (alcohol/water ratio: 90/10).

was investigated. Polymerizations were performed: with three different PAA concentrations (i.e., 0.5, 1.0, and 2.0 g/dL); within three dispersion media (i.e., Iso-PrOH/water, 1-BuOH/water, and 2-BuOH/water); with two different alcohol/water ratios (i.e., 70/30 and 90/10); at a constant initiator (i.e., AIBN) concentration of 1% (by mol); and at a constant monomer/dispersion medium ratio of 1.0/10.0. Table V gives the data obtained in this group of experiments. The SEM photographs of microbeads with different stabilizer concentrations in Iso-PrOH/water dispersion medium are exemplified in Figure 4. The variations of average particle diameter with stabilizer concentration for apolar (i.e., 90/10 alcohol/water ratio) and polar (i.e., 70/30 alcohol/water ratio) dispersion media are given in Figures 5 and 6, respectively.

As seen here, the average particle size decreased with increasing stabilizer concentration for all dispersion media. It may be explained by the fact that

dispersion polymerization begins and progresses around the stabilizer chains.²³ During the nucleation period, the stabilizer chains form a structure that acts as a skeleton for particle growth. The number of forming nuclei increases with increasing stabilizer concentration that leads to more particles but with smaller size.

The results indicated that the most proper dispersion medium for production of monosize PS microbeads was the isopropanol/water system. The variation of stabilizer concentration did not effect the monodispersity of PS microbeads in Iso-PrOH/water dispersion medium for both 70/30 and 90/10 alcohol/water ratios. But it should be noted that relatively smaller microbeads were obtained in this medium.

All of the dispersion media were homogeneous with 90/10 alcohol/water ratio at either room or polymerization temperature. The average particle size generally obeyed the following order with 90/

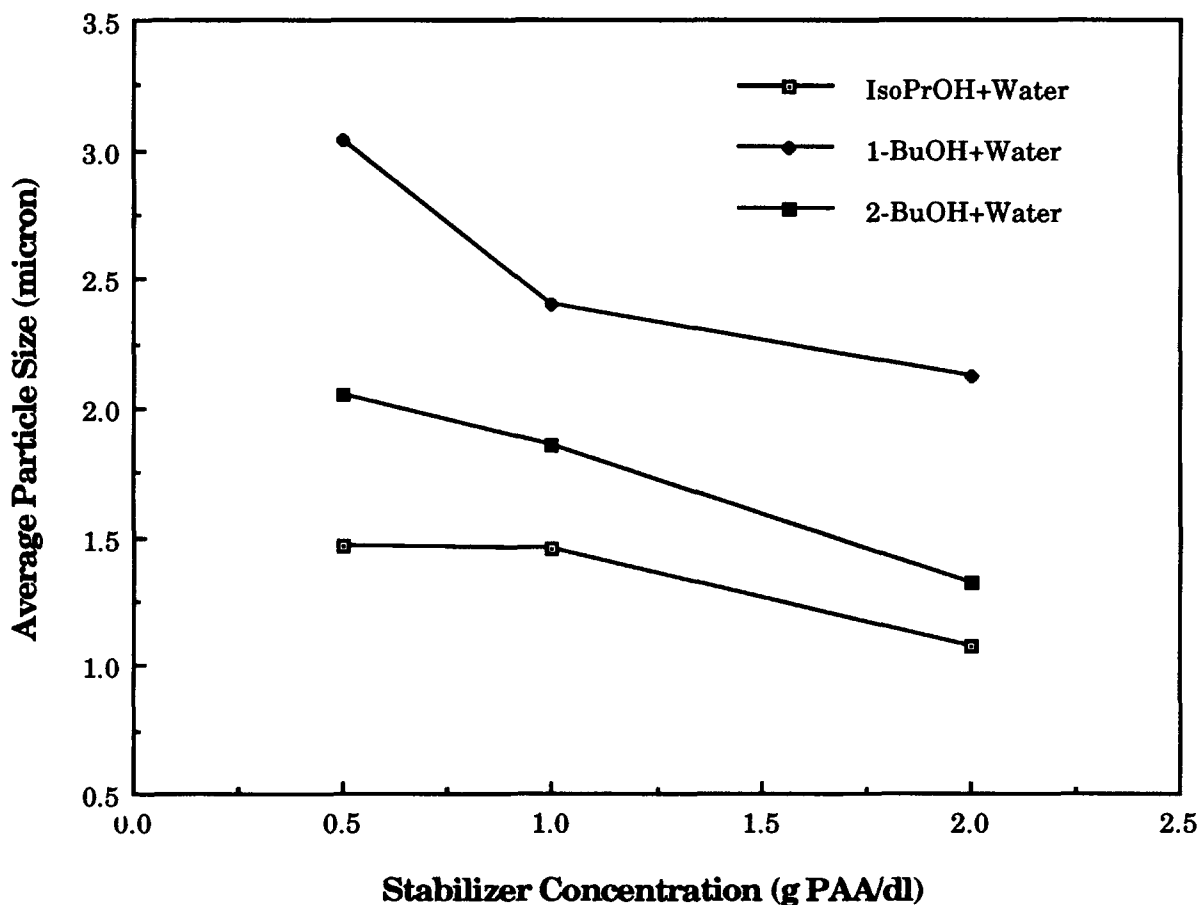


Figure 6 Effect of stabilizer concentration on average particle size (alcohol/water ratio: 70/30).

10 alcohol/water ratio, at a constant stabilizer concentration (Fig. 5).

2-BuOH/water > 1-BuOH/water
> Iso-PrOH/water.

The average particle size increased with decreasing polarity or decreasing solubility parameter of the dispersion medium at constant stabilizer concentration. However, it should be pointed out that, there were significant deviations from monodispersity in the cases in which 1-BuOH or 2-BuOH were utilized with 90/10 alcohol/water ratio.

The same average particle size order as in the initiator experiments was also observed for constant stabilizer concentration with 70/30 alcohol/water ratio. The largest microbeads were obtained in the 1-BuOH/water dispersion medium with this alcohol/water ratio (Fig. 6). Although a decrease was observed in the average particle size, the coefficient

of variation increased with increasing stabilizer concentration in this dispersion medium (Table V). Note that the size distributions obtained in the 2-BuOH/water system were narrower than those observed in the 1-BuOH/water with 70/30 ratio. The higher size distributions observed in the 1-BuOH/water system may be attributed to the more apolar character of the light phase in this system relative to that in the 2-BuOH/water. The homogeneous and most polar medium with 70/30 alcohol/water ratio (i.e., IsoPrOH/water) provided the smallest particles with reasonably narrower size distributions at constant stabilizer concentration compared to the other alcohol types.

Effect of Alcohol/Water Ratio

In this group of experiments, the effect of alcohol/water ratio on dispersion polymerization of styrene was investigated. Polymerizations were performed with five different alcohol/water ratios (i.e., 100/0,

Table VI Effects of Alcohol/Water Ratio on Average Size and Size Distribution

Dispersion Medium: Isopropanol/Water						
Alcohol/Water Ratio (mL/mL)	D (μm)	Dv (μm)	SD (μm)	CV (%)	Size Range (μm)	SSA (m^2/g)
100/0	2.02	2.06	0.312	15.46	1.37–2.46	2.85
90/10	1.89	1.89	—	—	MS	3.17
80/20	1.48	1.48	—	—	MS	4.05
70/30	1.46	1.46	—	—	MS	4.11
60/40	1.64	1.64	—	—	MS	3.58
Dispersion Medium: 1-Butanol/Water						
100/0	3.02	3.15	0.688	22.78	1.35–3.51	1.84
90/10	2.17	2.26	0.477	21.99	1.03–2.56	2.57
80/20	2.28	2.29	0.183	8.04	1.64–2.46	2.65
70/30	2.40	2.43	0.297	12.39	1.75–2.75	2.43
60/40	2.11	2.18	0.672	31.86	0.79–2.89	2.53
Dispersion Medium: 2-Butanol/Water						
100/0	2.012	2.10	0.433	21.54	1.12–2.69	2.75
90/10	2.34	2.41	0.429	18.32	1.35–2.70	2.43
80/20	1.73	1.73	—	—	MS	3.47
70/30	1.86	1.86	0.075	4.00	1.84–2.11	3.21
60/40	2.00	2.00	0.124	6.20	1.79–2.05	2.98

D: average diameter; Dv: volume average diameter; SD: standard deviation; CV: coefficient of variation; SSA: specific surface area; MS: monosize microbeads (CV < 1.0%).

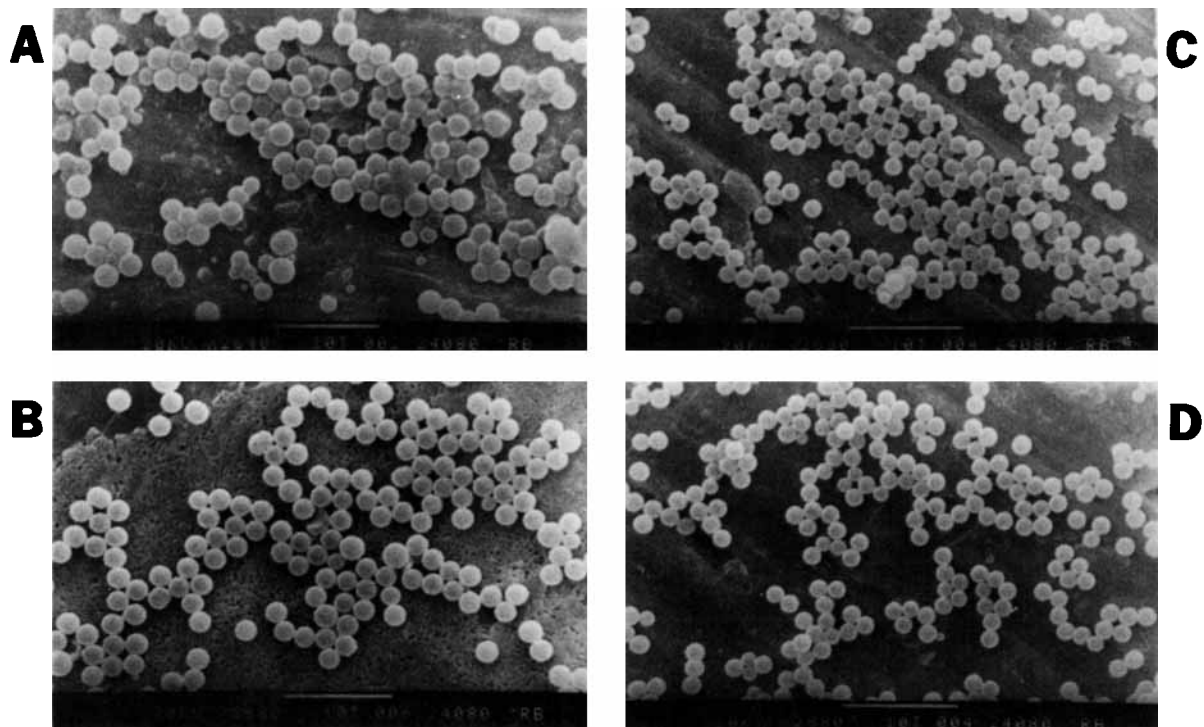


Figure 7 SEM photographs of microbeads with different alcohol/water ratios (in Iso-PrOH/water dispersion medium); (A) 100/0 Iso-PrOH/water; (B) 90/10 Iso-PrOH/water; (C) 80/20 Iso-PrOH/water; (D) 70/30 Iso-PrOH/water.

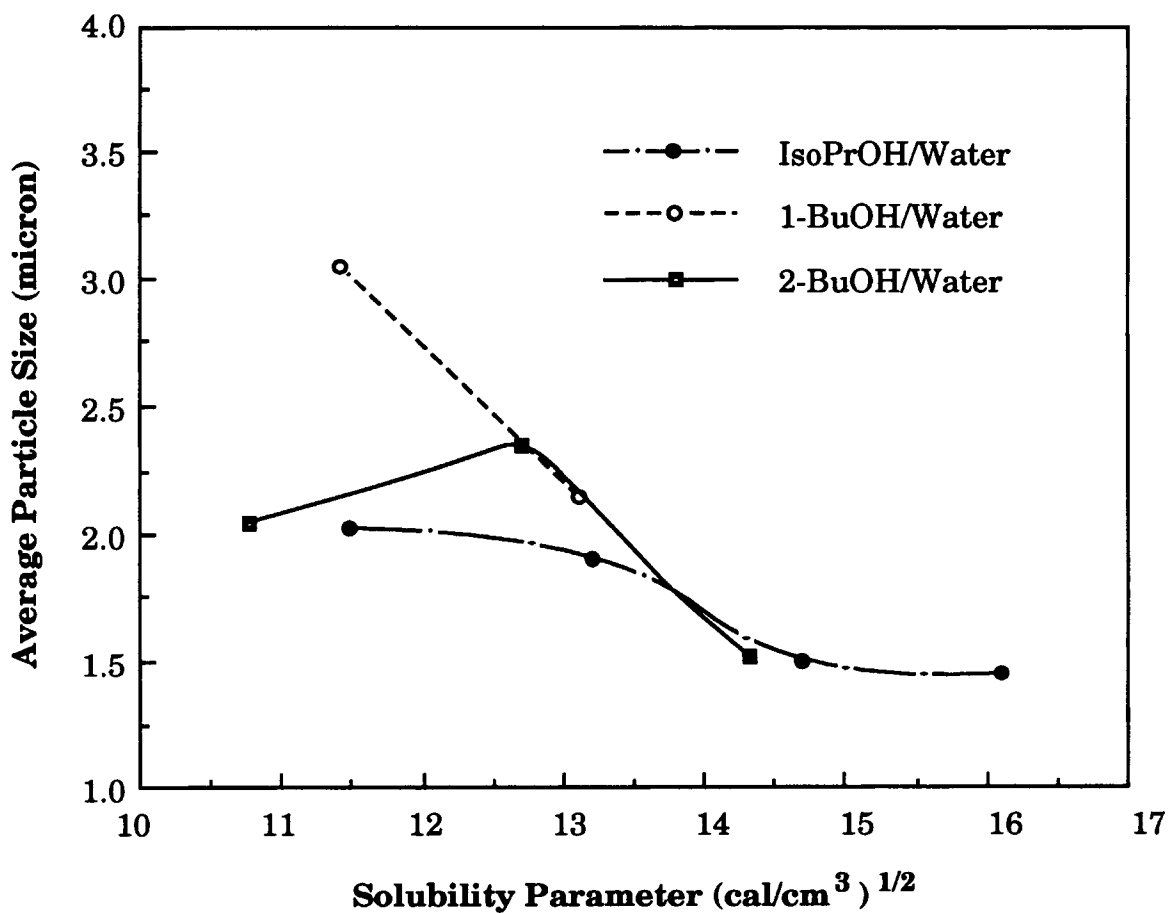


Figure 8 Effect of average solubility parameter of the dispersion medium on the average particle size.

Table VII Solubility Data of Dispersion and Polymerization Media for Different Alcohol/Water Ratios

Dispersion Medium	Alcohol/Water Ratio (mL/mL)	Dispersion Medium (Alcohol + Water)		Polymerization Medium (Alcohol + Water + Monomer) ^a	
		20°C	70°C	20°C	70°C
Iso-PrOH/Water	100/0	H	H	H	H
	90/10	H	H	H	H
	80/20	H	H	H	H
	70/30	H	H	H	H
	60/40	H	H	H	H
1-BuOH/Water	100/0	H	H	H	H
	90/10	H	H	H	H
	80/20	HT (94.5/5.50)	HT (95.0/5.0)	HT (92.5/7.50)	HT (97.0/3.0)
	70/30	HT (86.0/14.0)	HT (87.0/13.0)	HT (80.0/20.0)	HT (83.5/16.5)
	60/40	HT (67.0/33.0)	HT (69.0/31.0)	HT (69.0/31.0)	HT (71.5/28.5)
2-BuOH/Water	100/0	H	H	H	H
	90/10	H	H	H	H
	80/20	H	H	H	H
	70/30	H	H (97.5/2.5)	HT (82.0/18.0)	HT (84.0/16.0)
	60/40	HT (79.0/21.0)	HT (78.0/22.0)	HT (68.0/32.0)	HT (72.0/28.0)

H: Homogeneous medium; HT: Heterogeneous medium. The numbers in parentheses show the volumetric ratio of upper (light, apolar) phase to lower (heavy, polar) phase.

^a Monomer concentration was fixed to 10% (v/v) as in the polymerization experiments.

Table VIII Effects of Monomer/Dispersion Medium Ratio on Average Size and Size Distribution

Dispersion Medium: Isopropanol/Water							
Alcohol/Water Ratio (mL/mL)	Monomer/Dispersion Medium Ratio (mL/mL)	D (μm)	Dv (μm)	SD (μm)	CV (%)	Size Range (μm)	SSA (m ² /g)
70/30	1.0/10	1.46	1.46	—	—	MS	4.11
	1.5/10	1.80	1.84	0.254	14.13	1.49–2.16	3.22
	2.0/10	1.92	1.97	0.336	17.54	1.05–3.37	2.96
	2.5/10	Aggregation		—	—	—	—
90/10	1.0/10	1.89	1.89	—	—	MS	3.17
	1.5/10	2.13	2.13	—	—	MS	2.82
	2.0/10	2.52	2.95	0.301	11.96	1.12–2.67	2.32
	2.5/10	3.27	3.31	0.393	12.04	2.43–3.178	1.79
Dispersion Medium: 1-Butanol/Water							
90/10	1.0/10	2.17	2.26	0.477	21.99	1.03–2.56	2.57
	1.5/10	2.26	2.29	0.244	10.78	1.92–2.56	2.59
	2.0/10	3.23	3.32	0.607	18.77	1.05–3.68	1.77
	2.5/10	4.09	4.38	1.229	30.07	1.03–5.38	1.30
Dispersion Medium: 2-Butanol/Water							
90/10	1.0/10	2.34	2.41	0.429	18.32	1.35–2.70	2.43
	1.5/10	2.58	2.64	0.432	16.74	1.54–3.08	2.21
	2.0/10	3.05	3.18	0.683	22.39	1.28–3.59	1.82
	2.5/10	3.23	3.38	0.637	19.71	2.56–4.10	1.75

D: average diameter; Dv: volume average diameter; SD: standard deviation; CV: coefficient of variation; SSA: specific surface area; MS: monosize microbeads (CV < 1.0%).

90/10, 80/20, 70/30, and 60/40); within three dispersion media (i.e., Iso-PrOH/water, 1-BuOH/water, and 2-BuOH/water); at a constant stabilizer (i.e., PAA) concentration of 1.0 g/dL; at a constant initiator (i.e., AIBN) concentration of 1% (by mol); and at a constant monomer/dispersion medium ratio of 1.0/10.0. Table VI gives the data obtained in this group of experiments. The SEM photographs of microbeads prepared with four different alcohol/water ratios in Iso-PrOH/water are given as examples in Figure 7. The solubility characteristics of dispersion and polymerization media for different water contents are given in Table VII.

A wide size distribution was observed when pure isopropanol was utilized as the dispersion medium.

But monodispersity was achieved especially with 80/20 and 70/30 Iso-PrOH/water ratios. Note that both the dispersion and polymerization media were homogeneous in Iso-PrOH/water. The average particle size decreased with increasing water content (polarity) of the dispersion medium for the Iso-PrOH/water mixture. Because the oligomer chains formed during polymerization are relatively apolar, these chains can reach relatively higher molecular weights by remaining in the dissolved form in an Iso-PrOH/water medium having more apolar character (less water). Then nucleation occurs at relatively higher molecular weights due to the higher solubility of polymer chains in relatively apolar dispersion medium. Fewer nuclei will be produced and

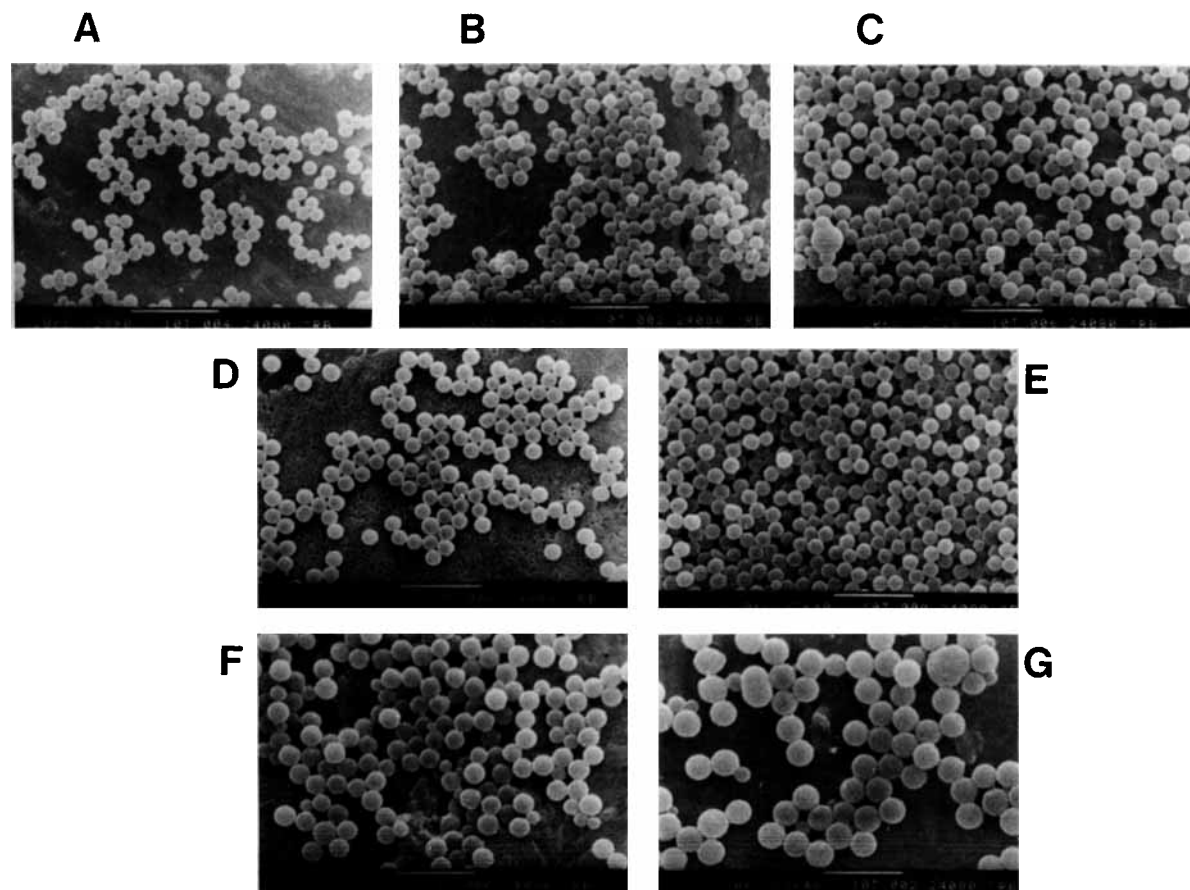


Figure 9 SEM photographs of microbeads with different monomer/dispersion medium ratio (in Iso-PrOH/water dispersion medium): (A) 1.0/10.0 mL monomer/mL dispersion medium, 70/30 Iso-PrOH/water; (B) 1.5/10.0 mL monomer/mL dispersion medium, 70/30 Iso-PrOH/water; (C) 2.0/10.0 mL monomer/mL dispersion medium, 70/30 Iso-PrOH/water; (D) 1.0/10.0 mL monomer/mL dispersion medium, 90/10 Iso-PrOH/water; (E) 1.5/10.0 mL monomer/mL dispersion medium, 90/10 Iso-PrOH/water; (F) 2.0/10.0 mL monomer/mL dispersion medium, 90/10 Iso-PrOH/water; (G) 2.5/10.0 mL monomer/mL dispersion medium, 90/10 Iso-PrOH/water.

the final particles will be of a larger diameter. The nucleation process occurs at lower molecular weights of oligomer chains due to the decreasing solubility of those in the dispersion medium with increasing water content. This effects leads to the generation of more particle nuclei and hence to smaller particles with increasing water content.

As seen in Table VII, a two phase formation was observed with increasing water content of dispersion medium in the 1-BuOH/water and 2-BuOH/water dispersion media. The particle sizes were possibly controlled by the average polarities of these two phases. The deviations from the tendency of decreasing particle size with increasing water content may be attributed to the heterogeneous character of the dispersion medium as discussed previously.

The variation of average particle size with the average solubility parameter of the dispersion medium is given in Figure 8. The average solubility parameters were calculated according to the following expression for only homogeneous dispersion media.²⁷

$$\delta_m = (x_a \delta_a^2 + x_w \delta_w^2)^{1/2} \quad (1)$$

where, x_a , x_w are the volume fractions of alcohol and water; δ_m , δ_a , and δ_w are the solubility parameters of the dispersion medium, alcohol, and water, respectively.

As seen in Figure 8, there is a certain relation between the polarity of the dispersion medium and the average particle size, when the alcohol/water mixtures are used as dispersion media. The average particle size generally decreased with increasing solubility parameter (=increasing polarity) of the dispersion medium for each alcohol type. Note that the average particle size values obtained by using pure 1-BuOH and 2-BuOH as dispersion medium deviated from this tendency.

Effect of Monomer/Dispersion Medium Ratio

In this group of experiments, the effect of monomer/dispersion medium volumetric ratio on dispersion polymerization of styrene was investigated. Polymerizations were performed: with four different monomer/dispersion medium volumetric ratio (i.e., 1.0/10.0, 1.5/10.0, 2.0/10.0, and 2.5/10.0); within three dispersion media (i.e., Iso-PrOH/water, 1-BuOH/water, and 2-BuOH/water); at a constant stabilizer (i.e., PAA) concentration of 1.0 g/dL. The initiator (i.e., AIBN) concentration was constant (1% by mol) in the Iso-PrOH/water and 1-BuOH/water,

but the amount of initiator was constant (0.07 g) in the 2-BuOH/water. Table VIII gives the data obtained in this group of experiments. The SEM photographs of microbeads prepared with different alcohol/water ratios, in the Iso-PrOH/water and 1-BuOH/water are exemplified in Figures 9 and 10.

Note that only the dispersion media showing homogeneous character at the polymerization temperature were studied in this group of experiments. All of the polymerization media prepared in this group of experiments were also homogeneous except 70/30 isopropanol/water medium with 25% monomer content in which an aggregation was observed. As seen in Table VIII, the average particle size and size distribution increased with increasing volumetric ratio of monomer/dispersion medium. In the Iso-PrOH/water system, PS microbeads with relatively smaller size, but narrower size distribution were obtained (Fig. 9). The largest microbeads (4.09 μm) were obtained in the 1-BuOH/water dispersion medium. In this medium, the monomer/dispersion medium ratio of 2.0/10.0 gave the average particle

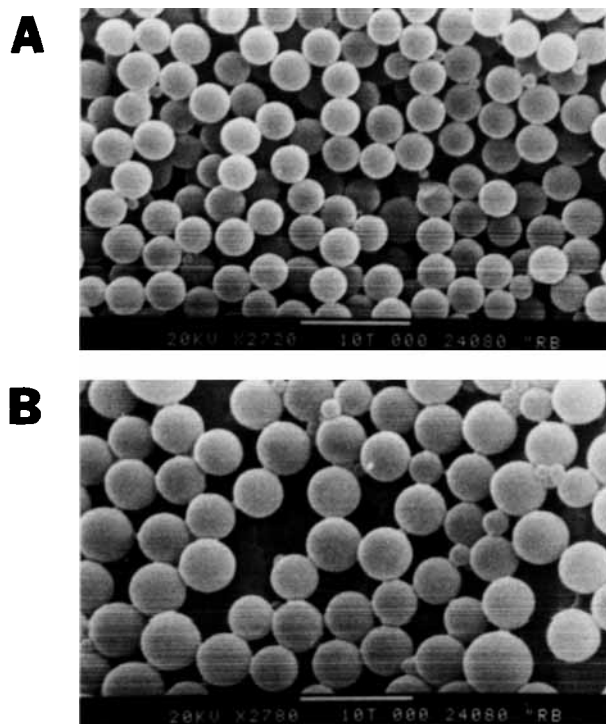


Figure 10 SEM photographs of microbeads having maximum average diameter obtained in this study (in 1-BuOH/water dispersion medium): (A) 2.0/10.0 mL monomer/mL dispersion medium; (B) 2.5/10.0 mL monomer/mL dispersion medium.

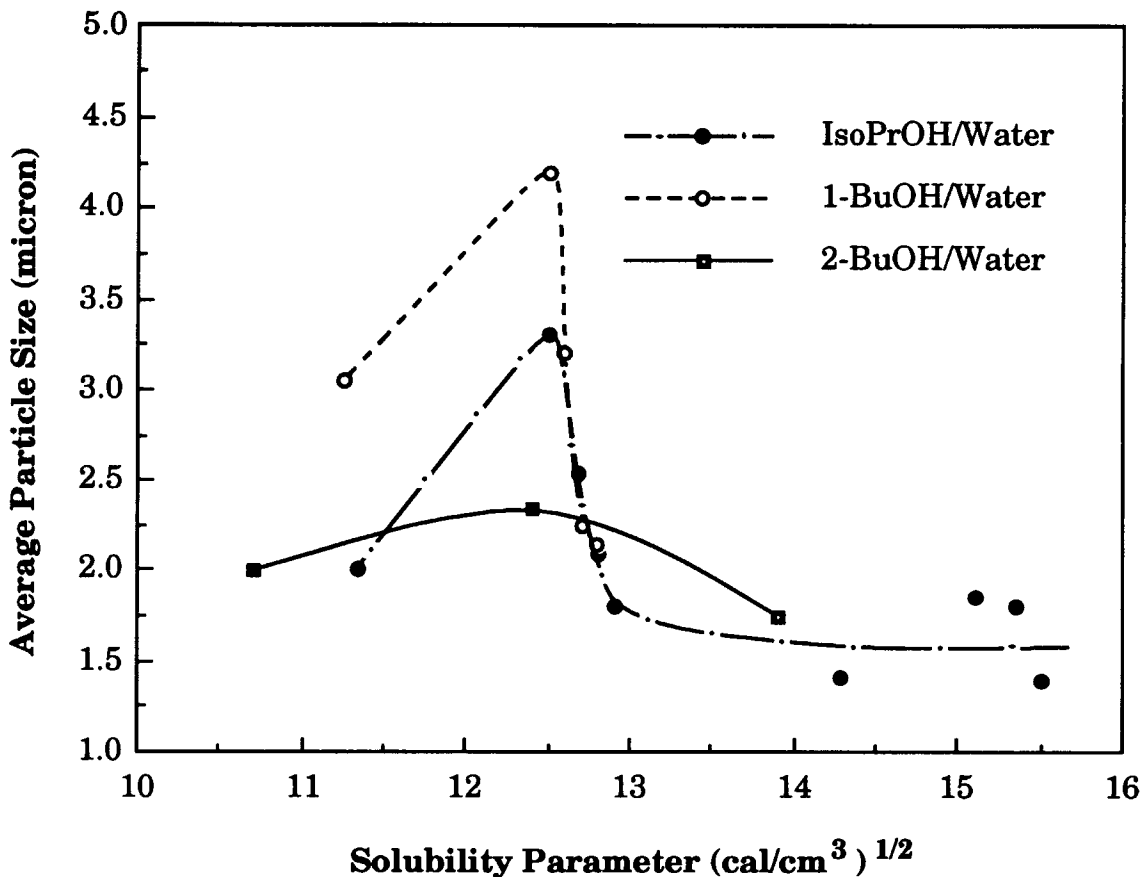


Figure 11 Effect of the average solubility parameter of the polymerization medium on the average particle size.

size of 3.23 μm with relatively narrow size distribution (Fig. 10). It should be noted that 2-BuOH/water dispersion medium is the most apolar medium, therefore one may expect that particles with the largest size should be obtained in this medium. However, due to a constant amount of initiator used in this group, the initiator concentration was relatively lower than the other dispersion media. Hence, lower initiator concentrations especially at higher monomer/water ratios resulted in smaller particles.

The variation of average particle size with the initial solubility parameter of the polymerization medium (including the solubility parameters of alcohol, water, and styrene) is given in Figure 11. A sharp decrease was observed in the average particle size in the solubility parameter range of 12.5–13.0 for especially Iso-PrOH/water and 1-BuOH/water dispersion media (Fig. 11). The maximum average particle size values for each alcohol/water system were obtained at an approximate value of solubility parameter of 12.5. However, the particle sizes ob-

tained by using pure alcohols as dispersion media deviated from the apparent tendency of decreasing particle size with increasing solubility parameter.

CONCLUSION

In this study, polystyrene microbeads in monosize form or with narrow size distribution and in the size range of 1.4–4.0 μm were obtained by dispersion polymerization of styrene carried out in different alcohol (i.e., Iso-PrOH, 1-BuOH, 2-BuOH)/water media. Effects of initiator and stabilizer concentrations, alcohol type, alcohol/water, and monomer/dispersion medium ratios on the size and size distribution of the microbeads were studied. Important results can be concluded as follows:

1. Initiator concentration is one of the main parameters that is effective both on size and size distribution of the microbeads. Larger

microbeads but with significant size distribution are obtained by using a higher concentration of initiator.

2. Stabilizer concentration should be optimized to achieve monodispersity and to control the size of the microbeads. An increase in the stabilizer concentration decreases the average size and size distribution of the microbeads.
3. Water is one of the key components to achieve monodispersity. However, the increase in the water content of dispersion medium increases the polarity of the dispersion medium that leads to a decrease in the average size of the resultant microbeads.
4. Polarity of the polymerization medium is controlled by the type and amount of alcohol and water and styrene content. Microbeads with highly monodispersed but with smaller size are obtained by increasing the polarity. When the polarity decrease the average size of the microbeads increases; however this leads a wider size distribution.
5. Homogeneity of the dispersion or polymerization media at polymerization conditions significantly affects the size and size distribution of the polymeric microbeads. Depending on the type of alcohol and the alcohol/water and monomer/water ratios, heterogeneous systems can be observed. It is not possible to obtain monosize microbeads in heterogeneous dispersion media.
6. Concentration of the monomer should be lower than a certain limit, which depends on nature of the medium, in order to prevent formation of a two phase system in the polymerization media. More importantly, the increase in the monomer content in homogeneous dispersion media causes an increase in the apolar character of the medium which, in turn results in larger microbeads but with an appreciable size distribution.

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